Infrared Absorption of the ν_3 Fundamental of Liquid and Solid CH₄ and CD₄†

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(Received 25 April 1963)

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The ν_3 fundamental of CH₄, CD₄, and solutions of CD₄ in CH₄ has been studied in the liquid and solid state from 105° to 28°K. The broad liquid-state absorption approximates the gas-phase vibration–rotation envelope in the wings, but has significantly more absorption at the band center. This deviation is consistent with the assumption that molecules in the liquid can undergo hindered rotation. One consequence of this model is that rotatory motion of molecules is in part librational in character and selection rules predict an intense Q branch and weaker P, R, S, and O branches. Another consequence is that the liquid environment may induce molecular dipoles causing Raman selection rules to be operative which contribute further to an intensification of the Q branch. The bandwidth decreases gradually with temperature but undergoes no discernable discontinuous change on passing through the freezing point, which suggests that rotatory motion persists in this solid phase. The bandwidth of the fundamental of liquid and solid CD₄ is narrower than CH₄ but behaves in a similar fashion with temperature. The band shape and position of ν_3 of CD₄ in solution with CH₄ is indistinguishable from that of pure liquid CD₄, and suggests that resonance broadening or coupling of rotatory motion is not important for this phase. In the solid state, however, the ν_3 bandwidth of CD₄ in the CD₄–CH₄ solution is slightly larger than the ν_3 bandwidth of pure CD₄.

INTRODUCTION

THERMODYNAMIC measurements show that CH₄ has a λ point at 20.4°K.[1] It has been suggested that molecular rotation occurs in the solid above this temperature.[2] Recently, it has been shown that the infrared absorption spectrum can be useful in the determination of the extent of rotation in simple liquid systems.[3] There is interest, therefore, in examining the infrared spectra of liquid and solid methane as a means of estimating the rotatory motion of molecules in these phases. Savitsky and Hornig[4] have examined the infrared spectra of the solid phases of CH₄ and concluded from the absence of observable rotational fine structure that a barrier in excess of several hundred wavenumbers must hinder molecular rotation. Their experiments were limited to sample temperatures no higher than 40°K which is considerably below the melting point (90.6°K).[1] Crawford, Welsh, and Harrold[5] have studied the Raman spectra of methane as a liquid and as a solid just below its melting point. They could fit a vibration–rotation envelope to the broad ν_3 band (stretching mode of F_2 symmetry) of the liquid and concluded that rotation was essentially free in this state. The Raman spectrum of solid methane could not be well resolved because of scattering, but the persistent broadness of ν_3 led these workers to conclude that rotational freedom was unchanged by solidification.

In an attempt to remove the apparent contradiction between the infrared and Raman results and to gain a better understanding of rotational motion in the condensed phases of methane, the present work was undertaken. The infrared absorption of ν_3 of liquid and solid CH₄, CD₄, and a solution of CD₄ in CH₄ will be described.

EXPERIMENTAL

The low-temperature cell used for the study of liquids and solids has been described previously.[6] For these experiments gaseous methane was first condensed to a liquid and then slowly solidified by lowering the temperature. The temperature of the cell for experiments at about 100°K was obtained by carefully adding small quantities of liquid argon to the Dewar. Temperatures below 77°K were obtained either by pumping on liquid nitrogen or using liquid neon or helium as the coolant. Two copper–constantan thermocouples were soldered to the sample compartment and one was embedded in a sapphire window which was in contact with the absorbing methane. Temperature measurement is believed to be within ±2°K. The gases used were reagent grade. CH₄ was obtained from Phillips Petroleum Company, and CD₄ with a specified isotopic purity of 99% was supplied by Volk Radiochemical Company. The spectral slitwidths were 2 cm⁻¹ and the frequency accuracy, limited by the broadness of the observed peaks, was ±5 cm⁻¹.

RESULTS

The spectra of liquid and solid methane are shown in Fig. 1. The CD₄–CH₄ solution spectra which were taken using a 150 μ spacer were 2.6 mole % in CD₄.

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[2] L. Pauling, Phys. Rev. **36**, 430 (1930).
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[4] C. B. Savitsky and D. F. Hornig, J. Chem. Phys. **36**, 2634 (1962).
[5] M. F. Crawford, H. L. Welsh, and J. H. Harrold, Can. J. Phys. **30**, 81 (1952).
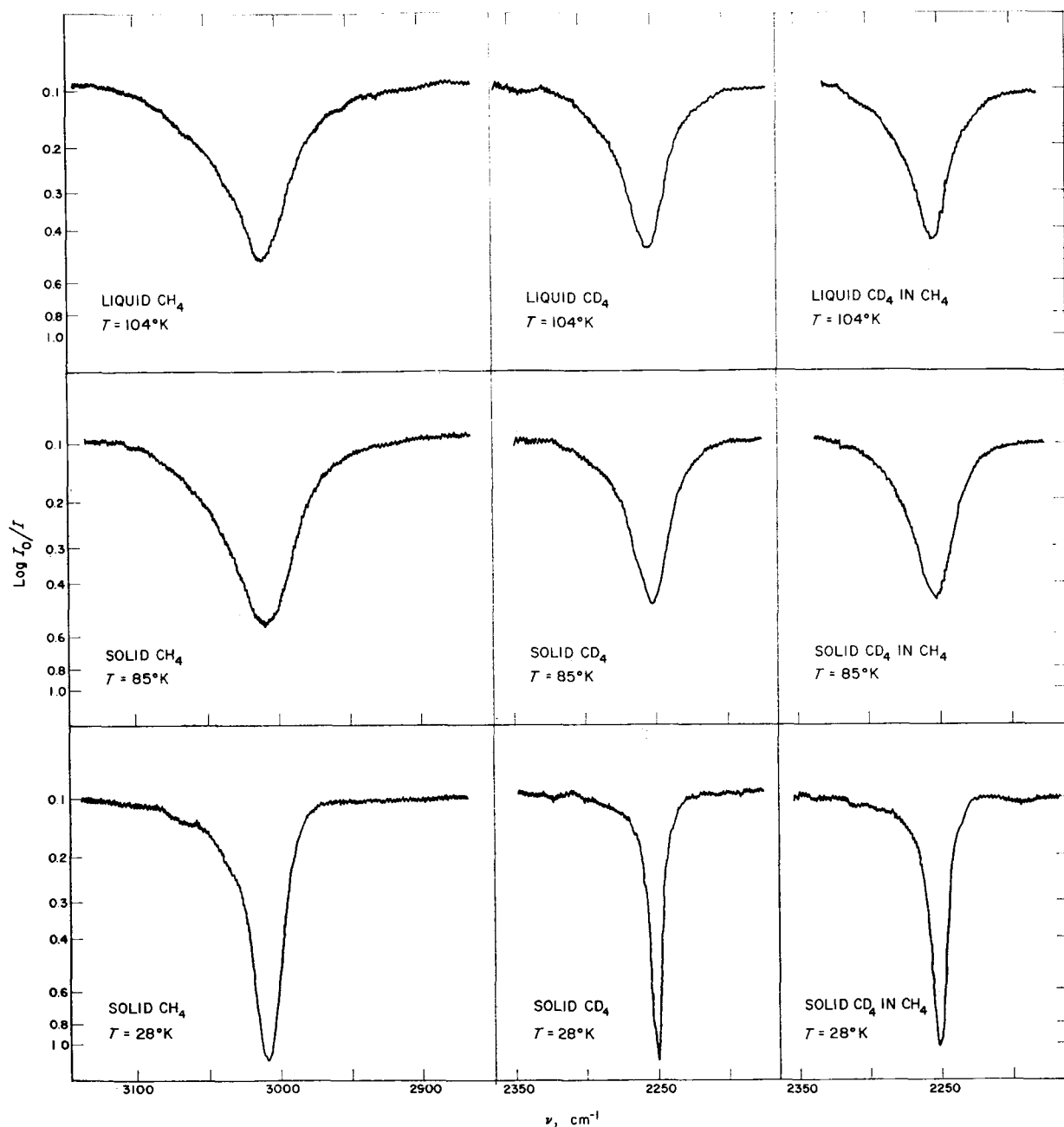[6] G. Ewing, J. Chem. Phys. **37**, 2250 (1962).

FIG. 1. Infrared absorption of ν_3 of liquid and solid CH_4, CD_4, and a solution of CD_4 in CH_4.

No spacer was used for the pure CH_4 and CD_4 spectra but an estimate based on the solution spectra intensity suggests that the path length was of the order of 3 μ.

The broad ν_3 absorption band for pure liquid or solid CH_4 is located at 3010 cm^{-1} ($\nu_{3\,gas}$ = 3020 cm^{-1}). The bandwidth is $\nu_{\frac{1}{2}}$ = 40 cm^{-1} at 105°K and decreases with temperature. The liquid- and solid-state spectra show only subtle intensity distribution differences near the melting point as shown in Fig. 2. The bandwidth of the solid decreases to $\nu_{\frac{1}{2}}$ = 15 cm^{-1} at 28°K. The small shoulder reported by Savitsky and Hornig[4] to

be on the high frequency side of the ν_3 absorption was not observed. In one experiment, the low-temperature solid phase of CH_4 was examined. With a small amount of liquid neon in the cold cell, the 28°K spectrum of CH_4 was recorded. Liquid helium was added on top of the neon until a temperature of 5°K was reached. The spectrum which was recorded showed the sharp features reported previously.[4] When the helium boiled off, a 28°K spectrum was again recorded which was indistinguishable from the earlier spectrum.

The ν_3 fundamental of CD_4 is centered at 2254 cm^{-1}

($\nu_{3\ gas}=2258$ cm^{-1}). The bandwidth ($\nu_{\frac{1}{2}}=26$ cm^{-1} at 105°K) is considerably narrower than that of CH₄, and decreases to $\nu_{\frac{1}{2}}=5$ cm^{-1} at 28°K. Spectra of the ν_3 fundamental of a 2.6-mole% solution of CD₄ in CH₄ are indistinguishable from pure liquid CD₄. The solid-solution spectral bandwidths are, however, slightly larger for the solution than the pure solid. This difference is particularly noticeable at 28°K.

DISCUSSION

Before discussing the infrared band shape of methane in terms of its freedom to undergo rotation in the liquid or solid state, it is important to review the effect intermolecular interactions would be expected to have on the vibration–rotation absorption. We therefore seek the influence of liquid environment on the vibration–rotation energy levels and the transition probability between them.

As a first approximation, liquid (or solid) methane is considered to be a system of independent hindered rotors. Each molecule is assumed to undergo rotatory motion in the presence of the perturbing influence of its neighbors. The spacing and degeneracy of the rotatory energy levels will depend on some periodic potential of the form $V = V(\theta+2\pi/l, \phi+2\pi/m, \chi+2\pi/n)$, where l, m, and n reflect the symmetry of the local environment. (See Fig. 5 of Ref. 6 for an energy diagram showing the effect of a qualitatively similar potential function on the rotatory energy levels of a liquid state molecule.)

If the barrier to rotation in the liquid, V_0, is small compared to the rotatory energy level, the environmental potential may be treated as a perturbation. The principal effect of the perturbation will be to split the $|m|$ degeneracy when the local symmetry is lower than the symmetry of the free-rotor wavefunction.[5] The magnitude of this splitting decreases with increasing J. The rotatory wavefunctions describing the system will deviate only slightly from the free-rotor wavefunctions of the gaseous molecule.

As V_0 gets large, the character of the rotatory motion changes until it is best described as librational.[6] The molecules make only small angular displacements from some equilibrium position. The resulting energy levels will be equally spaced and the wavefunctions will have the form of the harmonic-oscillator Hermite polynomials. The degeneracy of these low-lying librational energy levels, which depends on the local symmetry, will be split by tunneling through the potential barrier.

In order to determine the transition probability between the vibration–rotation levels it is necessary to calculate the electric dipole matrix elements,

$$\langle \mu_F \rangle = \langle \psi_v \psi_{N'} \mid M_F \mid \psi_{v''} \psi_{N''} \rangle + \langle \psi_v \psi_{N'} \mid P_F \mid \psi_{v''} \psi_{N''} \rangle,$$

$$(1)$$

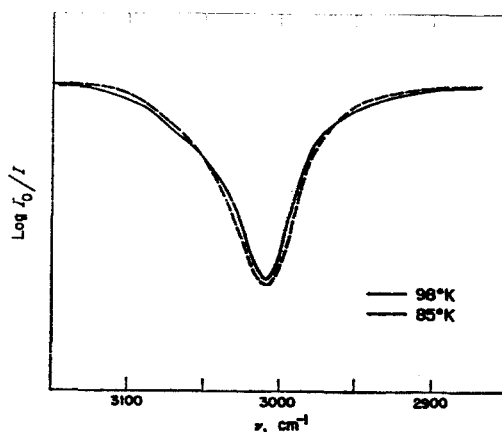for a given molecule in the liquid (or solid), where ψ_v

FIG. 2. A comparison of the ν_3 absorption of CH₄ above and below its melting point.

and ψ_N are the vibrational and rotational wavefunctions and $F=X$, Y, Z refers to the laboratory-fixed coordinate system. The dipole-moment operator is in two parts. The first term, M_F, is equal to that of an isolated gas-phase molecule. The second term, P_F, is the dipole moment induced in the given molecule by electric fields in the liquid produced by neighboring molecules.[7,8] It is difficult to assess a priori the relative importance of these terms. In explaining the ir spectrum of HCl dissolved in liquid argon, Kwok and Robinson[7] have suggested that the second term contributes very significantly to the absorption. A comparison of absorption intensity of liquid CO and N₂ suggests, however, that the second term is negligible compared to the first.[9]

If the liquid environment does not perturb the rotatory levels greatly (i.e. V_0 very small) then the gas-phase free rotar wavefunctions appropriate to methane may be substituted into (1). Since the band center for the gas-phase and condensed-phase absorptions differ by only 10 cm^{-1}, gas-phase vibrational wavefunctions will be used for ψ_v. The first term in (1) gives the usual ir selection rules, $\Delta J=0, \pm 1$ and $\Delta m = 0, \pm 1$. A calculation of the second term gives the usual Raman selection rules which are $\Delta J=0, \pm 1, \pm 2$; $\Delta m=0, \pm 1, \pm 2$. On the basis of the intensity distribution in the Raman vibration–rotation band of CH₄,[6]

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[7] J. Kwok and G. W. Robinson, J. Chem. Phys. 36, 3137 (1962).
[8] E. U. Condon, Phys. Rev. 41, 759 (1932).
[9] Since CO and N₂ are isoelectronic and have very similar physical properties, the polarizing influence of neighboring molecules would be expected to be about the same. In order to see comparable ir absorption with CO and N₂, path lengths required are, respectively, 10^{-3} and 1 mm[6]. By symmetry $M_F=0$ for N₂ and hence

$$\left[\int \ln\left(\frac{I_0}{I}\right) d\nu\right]_{CO} \bigg/ \left[\int \ln\left(\frac{I_0}{I}\right) d\nu\right]_{N_2}$$

$$= \frac{\mid \langle M_F \rangle + \langle P_F \rangle \mid^2}{\mid \langle P_F \rangle \mid^2} \sim 10^3;$$

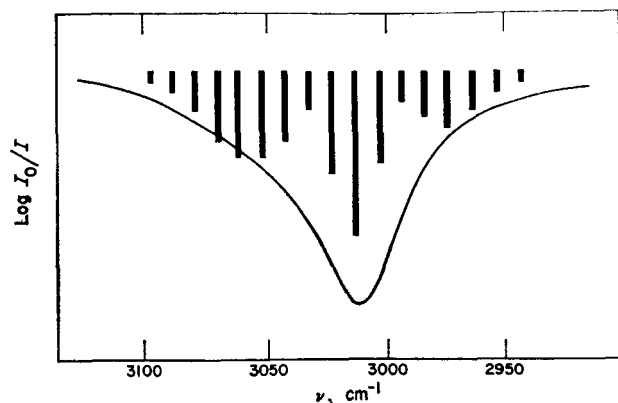therefore $\mid \langle P_F \rangle \mid < \mid \langle M_F \rangle \mid$.

FIG. 3. The ν_3 absorption of liquid CH_4 at 105°K and the theoretical gas-phase absorption.

the principle effect of polarization by the liquid environment will be to produce absorption which is concentrated at the band center and spread out far in the wings.

A high potential barrier to rotation in the liquid will cause the rotatory wavefunctions to be harmonic oscillator in type. Both terms in (1) will be nonzero only if $\Delta N = 0$, ± 1, ± 2, $\cdots$, decreasing in order of probability with increase in V_0 where N is the quantum number of the librational level.[6] The spectrum of a system of highly hindered rotors will have most of the absorption at the band center and decreasing amounts out in the wings.

In Fig. 3, the theoretical gas-phase spectrum of methane was fitted to the observed liquid-phase spectrum. The gas-phase vibration–rotation features are assumed to be triangular with $\nu_{\frac{1}{2}} = 25$ cm^{-1}. It was also assumed that spin equilibrium was not achieved. It is apparent that there is a very significant deviation between the gas- and liquid-phase spectra. The loss of rotational fine structure in the condensed state spectrum is the result of Stark-type splitting of the J levels induced by molecular collisions.[5] There is a reasonable agreement in the absorption in the wings for rotatory transitions originating about $J = 3$, but at the band center absorption is much greater in the liquid-phase spectrum. These observations are in agreement with those of Crawford et al.[5] If hindering barriers in the liquid giving rise to vibration–libration selection rules were alone responsible for the intensified Q branch then a barrier height of $V_0 \simeq E(J=3) = 63$ cm$^{-1} = 180$ cal/mole would be reasonable. However, polarization by the liquid may cause a considerable contribution of the second term in (1). In this case, even rotatory levels well above the barrier height V_0 will give absorption resulting in a strong Q branch (and weaker O and S branches) which overlap the R and P branches, thus distorting the band shape. The estimated barrier of 180 cal/mole must then be considered only an upper limit.

The bandwidth of CD_4 is considerably narrower than that of CH_4, as is expected from the difference in moment of inertia. The low-lying states which can be described as librational will have their energy levels[6] shifted by $1/\sqrt{2}$ on deuteration, while those levels well above the barrier will be shifted by $\frac{1}{2}$. Unfortunately, it is not possible to calculate the exact modification of the bandwidth by isotopic substitution since it depends in a complicated way on the spacing, degeneracy, and transition probability of the energy levels. It is interesting to notice, however, that the separation of the maxima of the P and R branches of an unresolved vibration–rotation band[10] (which roughly corresponds to $\nu_{\frac{1}{2}}$, see Fig. 3) would change by a factor of $1/\sqrt{2} = 0.71$ on deuteration. The observed ratio of bandwidths for CD_4 to CH_4 at 105°K is 40 cm^{-1}/26 cm$^{-1} = 0.65$.

The similarity in the spectra of liquid CD_4 and the solution of CD_4 in CH_4 adds support to the assumption that the liquid may be considered a system of *independent* hindered rotors. If coupling of rotatory motion were important, an alteration in bandshape of CD_4 would be expected in going from a system of CD_4 to CD_4 in CH_4, since the moment of inertia of the neighboring molecules is changed by a factor of 2.

The ν_3 absorption of methane 5° above or below the melting point shows only a slight difference in intensity distribution which is to be expected from the temperature change. The lack of gross band shape change suggests that solidification does not affect significantly the rotatory motion of the molecules. Furthermore, since the shape and height of the potential barrier is determined by the symmetry and spacing of the neighboring molecules,[6] the near-neighbor molecular arrangement in the liquid must be very similar to that of the solid. Thus the similarity of liquid spectra with that of the solid is consistent with the cluster model of the liquid state, as applied to the methane system.

As the temperature of the solid is lowered, the bandwidth decreases continuously. This is expected since the population of the high rotatory levels decreases. It is also possible that the potential barrier to rotation increases as the solid approaches the λ point. Recent calculations[11] suggest that the splitting of the low-lying rotatory levels of CH_4 by a potential barrier of 180 cal/mole would be of the order of 10 cm^{-1}. The narrow bandwidth observed at 28°K ($\nu_{\frac{1}{2}} = 15$ cm^{-1}) and the lack of observed librational structure suggest that the rotational barrier does increase as the temperature is lowered.

At low temperatures, the CD_4 bandwidth of CD_4 in CH_4 is noticeably greater than it is in pure CD_4. This may be explained by considering an absorbing

[10] G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Inc., New York, 1950) 2nd ed., p. 127.

[11] A. Cabana, D. F. Hornig, and G. B. Savitsky, Technical Report No. 15, ONR Contract NONK 1858 (27) NR–014–203, Princeton University.

CD$_4$ molecule surrounded by CH$_4$ molecules. These neighboring molecules will produce a range of interactions which depend on their angular orientations. The range of orientations and therefore the range of interactions will be greater for CH$_4$ than CD$_4$ since the CH$_4$ has a smaller moment of inertia. The observation that the solution system has a greater bandwidth than pure CD$_4$ is convincing evidence that resonance energy transfer does not play a significant role in the broadening mechanism for methane in its liquid or the solid phase above the λ point.

CONCLUSION

The observed spectra of liquid and solid methane do not conflict with the hypothesis that the molecules are undergoing hindered rotation in these phases. For the liquid, the rotatory levels above the barrier to rotation are populated and most molecules are nearly freely rotating independently of each other. The similarity in the spectra of liquid and solid methane near the melting point suggests that rotatory motion is relatively unaffected by this phase transition. At low temperatures in the solid phase, molecules are in their lowest rotatory levels and motion can best be described as librational. Polarization by neighboring molecules may cause a modification of vibration–rotation selection rules. This effect would result in an increased absorption at the band center.